

Effect of Some Ions on the Iodination of Aniline in Aqueous Solution

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ABSTRACT

Iodination of aniline is known to be catalyzed by various ions. Studies in the literature have involved measurement of specific reaction rates at various concentrations of ions but without regard to the variation in the pH of the reaction system. Since the rate of reaction depends very much on the pH of the reaction system, any determination of catalytic constant of various ions or a comparison of the catalytic constant of various ions or a comparison of the catalytic constants of various ions would lack significance unless the pH is maintained the same. Hence in the present study the catalytic constants of three ions of homologous series namely acetate, formate and propionate have been carried out at 25.0 °C, 30.0 °C, 35.0 °C, and 40.0 °C, as well as at pH 4.3 and 4.8.

Keywords: Kinetics, Iodination, Catalytic constant, Aniline, Effect of ions.

INTRODUCTION

Iodination of aromatic rings is an electrophilic substitution reaction with variety of application in organic synthesis particularly in the synthesis of pharmaceuticals¹⁻⁶. Aromatic iodides have been used in the synthesis of many interesting natural products⁷ and also as bioactive materials⁸. They also have importance in medicinal and pharmaceutical research⁹⁻¹⁰. Therefore among the halogenations of aniline, in particular iodination of aniline have been carried out.

Electrophilic aromatic iodination are known to be subject of many workers¹⁻¹⁶.

In present study, we have carried out quantitative studies on the relationship between rate constant of iodination of aniline and the percentage of aniline base in a buffer solution and have found that the rate constant varied almost linearly with percentage of aniline base. Since the latter depends on the pH of the solution any comparison of the effectiveness of different ions as catalysts for the reaction is meaningless unless the pH is maintained the same. Hence for quantitative comparison of

the catalytic effect of various ions, a study of the reaction at a fixed pH is absolutely necessary. This aspect has not been found in the earlier investigations. Such study has therefore been undertaken to compare the catalytic effect of formate, acetate and propionate ions at fixed pH values.

The pka value of anilinium ion is 4.58 at 25.0 °C, at pH 4.58. Hence the percentage of aniline base and anilinium ion are fifty each. Therefore the present work is carried out at pH 4.8 and pH 3.8 wherein the percentages of aniline base and anilinium ion are of comparable magnitude so as to provide fair chance for each of them to react with iodine and also to indicate any difference in the catalytic effect of the ions at different proportions of the aniline base. The ions selected namely formate, acetate and propionate are such as to enable us to study their catalytic effect near the pH 4.58. The pka values of the corresponding acids are 3.75, 4.76 and 4.87 respectively. These pka values are different enough for their ions to show their catalytic effect and yet close enough to each other that pH values 4.8 and 4.3 can be obtained by proper concentration of the acids and ions (bases).

For the comparison of catalytic constants of these ions (bases), it is proposed to maintain fixed pH and yet vary the ion (base) concentration on the basis of the Henderson equation $\text{pH} = \text{pka} + \log [\text{Ion}(\text{base}) / \text{[acid]}]$. The rate constants determined at various ion(base) concentrations are plotted versus the ion (base) concentrations and the slope of the curve is the catalytic constant for that particular ion (base). Such catalytic constants have been determined 25.0°C, 30.0°C, 35.0°C and 40.0°C.

In present work the ionic strength of the reaction medium has been maintained constant (0.5M) and concentration of the potassium iodide at ten times that of Iodine.

EXPERIMENTAL

Solutions

All the chemicals used in the present study, for the preparation of solutions were of analytical grade. Doubly distilled water was used for preparation of solutions.

Ions in the reaction system

By using the Handerson equation, the concentration of acetic acid, formic acid and propionic acid are calculated for the desired pH and desired concentration of the acetate, formate and propionate ions in the range of 0.025M to 0.125M. calculated quantities of these solutions when mixed with the Aniline and Iodine and diluted to the final volume, yield the desired pH.

Kinetic measurements

In a typical kinetic run for the catalytic constant, K_{acetate} of acetate ion at pH 4.8 and 25.0°C, the composition of reaction mixture is as follows : acetate ion 0.025M, acetic acid 0.023M, iodine 0.005M, aniline 0.005M, potassium iodide 0.05M, potassium chloride 0.325M. The stock solutions are maintained at 25.0°C in thermostat. After attaining the constant temperature, the various components are mixed according above composition and stop watch is simultaneously started. At various intervals of time an aliquote of 5.0 cm³ is taken into 20.0 cm³ 1N sulphuric acid to quench the

reaction. The unreacted iodine is titrated against the standard 0.01M sodium thiosulphate solution using semimicro burette reading upto 0.02 cm³, using freshly prepared starch as an indicator.

Similarly measurements are carried out at various concentrations of acetate ions. The plot of specific reaction rate against the concentration of ion yields a straight line, the slope of this line gives the catalytic constant, K_{acetate} for this ions. Similarly the catalytic constants K_{formate} and $K_{\text{propionate}}$ are determined. The specific reaction rates are also obtained at various temperatures and the energy of activation are determined.

RESULTS AND DISCUSSION

The specific reaction rate of Iodination of Aniline in presence of acetate ions (0.025M) at pH 4.8 and temperature 25.0°C was determined by titrating the unreacted iodine against 0.01M sodium thiosulphate solution using starch as an indicator. The various specific reaction rates are reproducible to ± 0.2 and hence the catalytic constants are accurate to within $\pm 2\%$. The plot of $1/(a-x)$ versus time is straight line and it indicates that reaction is first order in Iodine and aniline each. The overall reaction is second order. The specific reaction rate is found to be **1.07 M⁻¹min⁻¹**. Similar determinations were made at temperature ranging from 30.0°C to 40.0°C and acetate ion ranging from 0.050M to 0.125M by keeping pH 4.8.

The catalytic constant for acetate ions, K_{acetate} were evaluated by plotting the specific reaction rates against the concentrations of acetate ions in the reaction

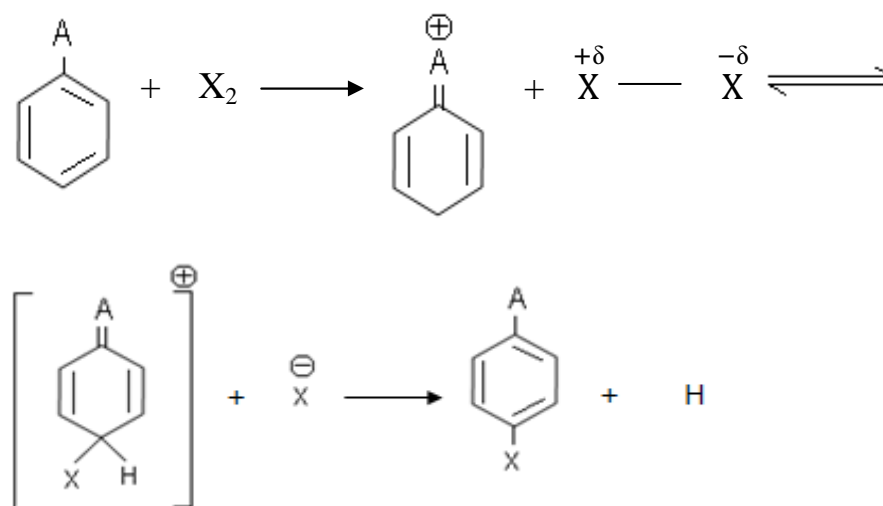
system. The plot yield a straight line and its slope is the catalytic constant, K_{acetate} . The value of K_{acetate} is found to be **9.6** at pH 4.8. Similarly catalytic constant determinations were made at temperature ranging from 25.0°C to 40.0°C and acetate ion concentration ranging from 0.025 M to 0.125 M at pH 4.3.

The above catalytic constant determinations were also made for formate and propionate ion either otherwise at identical conditions. (Table 1)

In present study the catalytic constant of the acetate, formate and propionate ions have been obtained strictly under constant pH values i.e. 4.8 and 4.3 although their concentrations were varied over a wide range from 0.025M to 0.125M in each case. Therefore catalytic constant of these ions enable us to compare their catalytic effects on a more rational basis.

The generally accepted mechanism of halogenations of aromatic substrates consists of formation of adduct which is followed by deprotonation.

Among halogenations in chlorination and bromination reactions the deprotonation is the faster one¹. While Iodination is exceptional, in which the deprotonation takes place at very slower rate and hence in Iodination deprotonation is the rate determining step. This step involves the breakage of a C-H bond in the aromatic ring²⁻³. It is because of this situation that the Iodination is highly susceptible to catalysis by acetate, formate and propionate ions, which are acting as a bases.

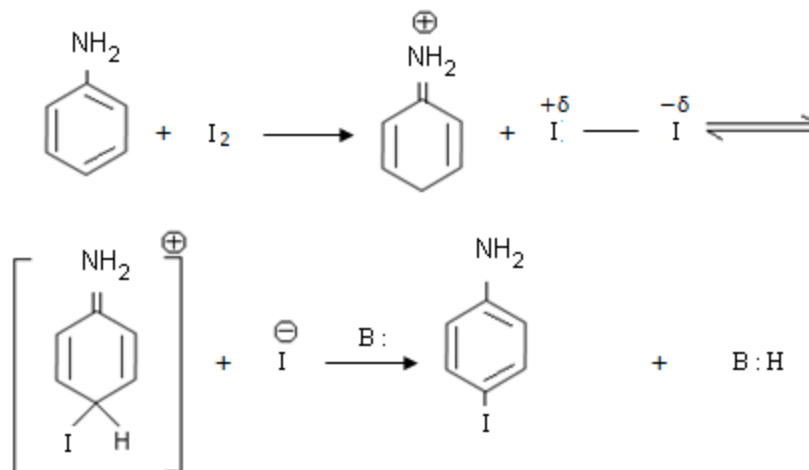


The results obtained in Table 1 shows that at a given pH and temperature, the relative values of the catalytic constants of the acetate formate and propionate ions are such as to be expected from the Bronsted relation⁴, $K_{\text{acetate/formate/propionate}} = G(1/k_a)^\beta$ where $K_{\text{acetate/formate/propionate}}$ is the catalytic constant for the catalysis by acetate formate and propionate ions and G and β are the constants for the similar catalysis by other ions but depends on the nature of the reaction and also on the solvent and temperature. K_a is the conventional strength of acid corresponding to ions.

On the basis of above relation, the formate ion has an exceptionally high catalytic constant, although belonging to the homologous series of the acetate and propionate ions considering the pK_a value of formate ion i.e. 3.75, the value of catalytic constant for formate ion should have been lower than that of catalytic constant of the acetate and propionate ions. This is

presumably because of the lack of any alkyl group on the carboxylic carbon enables the formate ion to approach the reactive site and form the product more readily than the acetate and propionate ions. The energy of activation for the Iodination of Aniline in presence of acetate, formate and propionate ions at pH 4.8 and pH 4.3 are found to be approximately same (Table 2). This indicates that the mechanism of catalysis by these ions is almost same.

The results presented in Table 1 clearly shows that the K_{acetate} , K_{formate} and $K_{\text{propionate}}$ varies with temperature and pH. At higher pH the catalytic constant for given ion is found to be more than at lower pH. This is because at higher pH there is higher concentrations of the ions as compared to acid. It is also observed that catalytic constant for these ions is higher at higher temperature than at lower temperature. This is due to the faster rate of deprotonation at higher temperature.



(B : = Acetate or formate or propionate)

Table 1 : Catalytic constant of various ions at different pH and temperatures for Iodination of Aniline.

Sr. No.	Temperature t/ °c	catalytic constant					
		K _{acetate}		K _{formate}		K _{propionate}	
		pH=4.8	pH=4.3	pH=4.8	pH=4.3	pH=4.8	pH=4.3
1	25	9.6	1.8	30.0	10.0	7.0	3.80
2	30	10.2	5.2	70.0	22.0	18.0	6.80
3	35	22.0	8.6	140.0	50.0	41.0	17.0
4	40	39.0	20.2	300.0	185.0	89.0	33.0

Table 2 : Iodination of Aniline : energy of activation.

Sr. No.	Ion	Energy of activation, Ea/kJ	
		pH=4.8	pH=4.3
1	Acetate	21.5	24.0
2	Formate	19.0	18.0
3	Propionate	16.6	16.9

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